Notes (*combined from several contributors*) on the Contributions to the Phased Approach Step 1:

Commented [WU1]: d'Almeida, Carolyn K. <dAlmeida.Carolyn@epa.gov>; Brasaemle, Karla <KBrasaemle@TechLawInc.com>; Davis, Eva <Davis.Eva@epa.gov>; Henning, Loren <Henning.Loren@epa.gov>; Arvind Kutty <AKutty@TechLawInc.com>; Cosler, Doug <DCosler@TechLawInc.com>; Wayne Miller (Miller.Wayne@azdeq.gov); Eleanor Jennings <ejennings@teci.pro>; Steve Willis <steve@uxopro.com>

Why are regulators proposing a phased implementation?

- Site conditions have changed from those contemplated in the ROD for EBR/MNA

- EBR/MNA has not been tested and proven effective at a site of this size, complexity, and source mass – particularly in terms of the timeframe contemplated, so a phased approach (i.e., with limited parts of the site being used for testing the proposed EBR approach, instead of immediately implementing full-scale EBR site-wide) is appropriate

- Therefore, a phased implementation (initially limited in terms of the volume of the subsurface applied) is indicated for refinement of the site model, refinement of performance criteria and trigger points, development of confidence limits around the remedial timeframe estimates, and to provide data for EBR design and operation (such as sulfate injection solution concentration, injection well spacing, potential usefulness of bioaugmentation, etc.).

- Incorporate 1 year pilot test in specified areas differentiating between heavy LNAPL areas and dissolved phase areas in LSZ,UWBZ and CZ

Commented [WU2]: We may need to list some of these changed site conditions, and prepare evidence for their existence, and importance to the path forward. AF has been arguing that in fact the current site conditions are basically what was expected, and therefore there is nothing really new that has to be considered – so we have to have our evidence ready.

Commented [WU3]: Note that AF is likely to say that this is basically what they are planning to do already.

That is, for example, in the Decision Tree, AF proposes this:

Decision Objective: To establish location is ready for EBR injections

Parameters will be evaluated in different areas of the site and may not be demonstrated everywhere simultaneously. Expansion of ideal conditions to all desired treatment areas will be part of the optimization step

So AF could say that they are already planning this kind (or somewhat similar kind) of phased implementation. But they are proposing their phased approach from an operational standpoint (i.e., tweaking and stepping operations), whereas we are proposing our phased approach from a testing standpoint (i.e., to test if EBR, as they propose it, will work). (Note that this is not a great explanation of the differences between the two approaches, but I anticipate that AF will say that they already plan to do all the "phased approach" that is necessary, and that in fact their plan will do everything needed, if not everything we ask for. I know it's not the same, but they are likely to contend that it is basically the same.)

Modeling

AF should provide a predictive modeling approach suited to determining timeframes for EBR and MNA to reach the respective goals for those remedy approaches. This modeling will include items related to performance criteria (timelines, triggers for determining remedy failure, COC concentrations, etc.).

ADEQ is working on alternative model/critique of AF model.

All models should do sensitivity analyses of major parameters.

Commented [WU4]: AF simultaneously denies and claims that their models) can predict timeframes.
If timeframes are important, then AF has to do modeling appropriate for high quality estimates of timeframes.

I suspect a large part of our effort here will have to be based on a detailed critique of their (rather simplistic) model. As Doug pointed out, the assumption of equilibrium between COCs in LNAPL and GW, the use of very low Foc (fraction of organic carbon) values, the use of the same effective porosity for all layers of the model, etc. are significant problems.

DC says: "it appears they have made a major assumption in the chemical transport and MNA models that assumes an equilibrium exists between pore-water concentrations and LNAPL. This means, for example, that groundwater in contact with NAPL will contain solubility levels (reduced by the mole fraction in the NAPL) of BTEX-N constituents.
It is well known that mass transfer limitations in NAPL source areas cause these concentrations to be much less in most cases. If that is the case in their modeling, then the models would overpredict (potentially significantly) BTEX mass removal by MNA. It also seems like they are using concentration threshold (e.g. benzene) criteria for stopping MNA activities, whereas it is not clear how much LNAPL would remain in the soil.
They also apparently assume equilibrium portioning between soil and groundwater, but this is typically not the case in real field conditions (e.g., the pump and treat "tailing effect", which is due to rate-limited desorption from low-permeability zones). They also appear to have significantly underestimated the amount of BTEX-N mass sorbed to soil because the fraction of organic carbon (foc) value they used (0.0003) is much less than what the sorption model (foc – koc model) is designed for (research shows that foc=0.001 is about the lowest value that should be used, because other sorption mechanisms take over when foc is low). ...

Laboratory Testing of Potentially Critical Factors

Perform lab testing to evaluate impact of temperature and sulfate loading rates on microbial population

Could do some lab studies to see reactions of the indigenous microbes to high sulfate/salinity; changes in populations (of sulfate reducers, particularly, to see if population drop sharply, rebound, etc.) and if TPH and the COCs are degraded over time. Use subsurface media samples (each sample with matrix, groundwater, LNAPL; use replications to establish variability of results) taken from the location where the Field Study is to be done.

Commented [WU5]: We need a list of proposed microbiological-related analyses for lab and field work. We have to provide evidence for why these analyses are needed, and specifically how they will be used to make particular decisions, and what could/would happen if that data were not available to support site decisions.

The decision criteria would include at least:

- the specific decisions to be made based on each analysis, and

- the values (or range of values), for each type of test, that determine the decisions(s) made

I assume AF will argue that:

- No useful decision can be made based on any particular analysis we propose (so we have to provide specifics of particular decisions to be made based on results of each analysis);

- Decisions are made based on a weight of evidence approach anyway, so any particular proposed analysis adds little if anything to the weight of evidence;

- No, or very few, pre-full-scale analyses need to be done, because the only thing that matters is what happens after EBR begins to be implemented (i.e., after sulfate injections, and etc. that change the geochemistry/microbiology are initiated). So we have to show specifically why the pre-implementation data is **very likely** to affect **remedy success**. Showing this may not be easy, but it is exactly what management needs to prevail in a dispute (Loren basically said that **we must be able to show that EBR will not succeed without our additions**, not that we just don't like the way EBR is proposed to be done, or that maybe it could be done better).

Pre-injection Analyses

Have AF propose their ideas for pre-injection analysis to assess microbiology and geochemistry initial conditions, for comparison to post-injection analyses.

We can propose our own pre-injection analyses to assess microbiology and geochemistry initial conditions, and try to come to a meeting of the minds with AF.

These pre-injection and post-injection tests (for the phased implementation) would form another set of performance criteria; that is, to determine if the appropriate microbe populations are developed to proper levels and activity.

Phased Implementation

A phased implementation, applied to a limited area of the site (but all vertical zones) would be the first major milestone (performance criterion) for success; i.e., if the COCs concentrations are lowered to the required concentrations, and stay there, that would be a major step to indicate feasibility of EBR to achieve RAOs.

Incorporate 1 year pilot test in specified areas; separate areas should be chosen in each of the LSZ, UWBZ, and CZ, so as to be representative of 1) high-LNAPL-content areas, and 2) groundwater-dissolved-only phase areas (i.e., six areas).

3-6 months of EBR testing should be sufficient to evaluate COC degradation rate in dissolved phase areas; up to a year may be necessary to evaluate COC degradation rate/LNAPL depletion rate in high LNAPL areas.

Commented [WU6]: I think that AF intends to get the COCs down to 500-600 ug/L so that MNA can complete the remediation to MCLs in the required timeframe.

Of course that means that the MNA part is also significantly uncertain (i.e., a whole different bag of uncertainty), even if EBR performs just like AF models it.

Commented [WU7]: It appears, as AF indicated in the conference call of March 16, 2017, that they perceive that there are no LNAPL goals set forth in the ROD. So it's only GW concentrations of BTEX+N.

AF claims that they don't actually have to get rid of LNAPL, but merely get GW concentrations of BTEX down to MCLs, "eventually". Encapsulation of LNAPL by microbial films (to degrade the BTEX moving from LNAPL to GW), by iron sulfide precipitates (to reduce flux of BTEX from LNAPL to GW), fouling and precipitates in and around LNAPL bodies (so that GW doesn't really flow close to the LNAPL) are things that could cause GW concentrations of BTEX to fall, while much BTEX remains in the remaining LNAPL. Hence my continued insistence on the idea that the details of performance monitoring make a huge difference in what "success" is.

Observation (performance monitoring) wells should spaced within 6 months groundwater travel time of injection wells; bromide or other conservative tracer should be used for evaluating flow distribution around injection wells, travel time to observation wells, COC/sulfate disappearance, and geochemical footprint of treatment zone.

The downgradient observation wells can not only monitor COC changes, but also assess the geochemical footprint of downgradient locations, which would be pertinent to evaluating possible enlargement of a sulfate/etc. plume at full scale.

Reagent injections (sulfate, etc.) should reflect those concentrations, rates, volumes, etc. that are proposed for full-scale EBR.

Assuming the phased implementation continues for at least a year, the changes around the injection wells in terms of microbiology, sulfate concentrations, sulfide production, hydrogen sulfide generation, precipitation of iron sulfides, possible aquifer plugging, changes in pH, etc., can be monitored and evaluated for viability of a full-scale remedy, and any likely dangers, showstoppers, etc.

Fouling should be assessed for all wells (injection, LNAPL, monitoring), to determine the likely needs for well reworking, refurbishing, eventual replacement, etc. This is particularly important for the follow-on contractor (after AMEC's contract expires) to have an idea of long-term costs, and how to bid.

Commented [WU8]: Appropriate monitoring will likely require installation of additional wells.

Grid the full treatment area into optimization zones based upon existing conditions identified during characterization:

- Heavy LNAPL vs dissolved phase,
- temperature,
- microbial population,
- available sulfate, etc. for optimized treatment, including possible bioaugmentation.

Install or designate observation wells within gridded optimization zones to evaluate remedy progress

Commented [WU9]: The distribution and concentrations of sulfate achieved downgradient of the injection transect is of great interest. The AF model indicates they can get a reasonable (to them) sulfate distribution, but reality in subsurface environments is often different from the models. The field study should designed to provide suitable data to design injection well spacing, injection rates, injection concentrations, pressures, etc., so as to achieve useful sulfate concentrations across the site.

From: d'Almeida, Carolyn K. [mailto:dAlmeida.Carolyn@epa.gov]
Sent: Friday, March 17, 2017 1:12 PM
To: Davis, Eva; Dan Pope; Brasaemle, Karla; Henning, Loren; Arvind Kutty; Cosler, Doug; Wayne Miller (Miller.Wayne@azdeq.gov)
Subject: RE: don't you need a predictive model slide 41

Also review of documents demonstrate progressively backing off or previous commitments:

- SEE to remove "most" of the LNAPL stated in draft Proposed Plan; evolved into system performance criteria in subsequent documents
- SEE Shutdown/EBR transition criteria specified in 2014 Final RDRA work plan were not met; excuse that mass outside the TTZ preventing attainment of objectives was a known factor at the time transition criteria were developed.
- 2014 RDRA workplan specified 12 weeks post SEE extraction; but terminated and dismantled after only 8 weeks
- 2014 Final workplan specified cell phone lot wells and wells on affected adjoining properties would be connected to extraction system via underground piping for containment during EBR which would run "longer than SEE" Concern about containment having adverse effect on biodegradation was not brought up in 2014 workplan.
- 2014 RDRA workplan specified 60' well spacing in 5 point injection pattern, as indicated by model to be optimal for amendment distribution (not to exceed 75' spacing). 61 EBR injection wells proposed in 2014 RDRA workplan, Reduced to 18 wells in 2016 Addendum 2 RDRAWP; no explanation provided for the reduction of injection wells.
- Model previously given as justification that remedy can meet RAOs, now told it can't be used to predict outcome, only a tool to understand process.

From: d'Almeida, Carolyn K. [mailto:dAlmeida.Carolyn@epa.gov]
Sent: Friday, March 17, 2017 5:10 PM
To: Dan Pope; Davis, Eva; Brasaemle, Karla; Henning, Loren; Arvind Kutty; Cosler, Doug; Wayne Miller (Miller.Wayne@azdeq.gov)
Cc: Eleanor Jennings; Steve Willis
Subject: RE: DFP Notes on the 3/17/2017 WAFB Conference Call

My notes from today:

- Adopt Phased Approach to implementation to collect site specific data to refine model, remedial timeframe estimate and performance criteria.
- Collect samples for microbial analysis to determine bacteria present, evaluate need for bioaugmentation.

- Perform lab testing to evaluate impact of temperature and sulfate loading rates on microbial population
- Incorporate 1 year pilot test in specified areas differentiating between heavy LNAPL areas and dissolved phase areas in LSZ,UWBZ and CZ. 3-6 months should be sufficient to evaluate degradation rate in dissolved phase areas, up to a year to evaluate degradation rate in heavy LNAPL areas. Will need observation wells spaced within 6 months travel time of injection wells; bromide tracer useful for evaluating flow distribution around well.
- Evaluate if amendment is achieving biodegradation or not
- Update model to verify remedial timeframe, performance evaluation criteria and optimize full scale implementation
- ADEQ working on alternative model

From: Cosler, Doug [mailto:DCosler@TechLawInc.com]
Sent: Thursday, March 16, 2017 1:30 PM
To: 'd'Almeida, Carolyn K.'; Henning, Loren; Davis, Eva; Dan Pope; Brasaemle, Karla; Kutty, Arvind
Cc: Anderson, Michael
Subject: RE: March 2017 BCT regulatory call

I've only about 3 hours today reading through various modeling reports, but it appears they have made a major assumption in the chemical transport and MNA models that assumes an equilibrium exists between pore-water concentrations and LNAPL. This means, for example, that groundwater in contact with NAPL will contain solubility levels (reduced by the mole fraction in the NAPL) of BTEX-N constituents.

It is well known that mass transfer limitations in NAPL source areas cause these concentrations to be much less in most cases. If that is the case in their modeling, then the models would overpredict (potentially significantly) BTEX mass removal by MNA. It also seems like they are using concentration threshold (e.g. benzene) criteria for stopping MNA activities, whereas it is not clear how much LNAPL would remain in the soil.

They also apparently assume equilibrium portioning between soil and groundwater, but this is typically not the case in real field conditions (e.g., the pump and treat "tailing effect", which is due to rate-limited desorption from low-permeability zones). They also appear to have significantly underestimated the amount of BTEX-N mass sorbed to soil because the fraction of organic carbon (foc) value they used (0.0003) is much less than what the sorption model (foc – koc model) is designed for (research shows that foc=0.001 is about the lowest value that should be used, because other sorption mechanisms take over when foc is low).

All of these factors would cause the "true" future concentrations to be higher than what their models predict.

I'm just getting up to speed, so we can discuss these and other issues on Friday.

Doug

From: Wayne Miller [[HYPERLINK "mailto:Miller.Wayne@azdeq.gov"]]
Sent: Thursday, March 2, 2017 4:04 PM
To: d'Almeida, Carolyn K. <[HYPERLINK "mailto:dAlmeida.Carolyn@epa.gov"]>
Cc: steve <[HYPERLINK "mailto:steve@uxopro.com"]>
Subject: 2017-3-2 - Williams AFB - FYI - Eleanor Jennings TEC for UXO Pro- sulfate injection perspective - USAF moving EBR forward - response to PMook Feb 10 ST012 -

FYI - Some perspective points and opinions provided by Eleanor Jennings (with TEC for UXO Pro, Inc.). Eleanor's comments are in purple and follow Dan Pope and Eva Davis discussion (Feb. 27-28, 2017).

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Excerpted From Dan Pope and Eva Davis (Emails Feb 27-28, 2017)

From: Davis, Eva [[HYPERLINK "mailto:Davis.Eva@epa.gov"]]
Sent: Tuesday, February 28, 2017 9:47 AM
To: Dan Pope; d'Almeida, Carolyn K.
Cc: Henning, Loren; Wayne Miller ([HYPERLINK "mailto:Miller.Wayne@azdeq.gov"])
Subject: RE: Sulfate Distribution

The figure was just E-21 from the Draft_Final_ST012_RD-RAWP_Addendum2.pdf.

According to the AF response*, Assuming most of the sulfate is converted to sulfide by the EBR process (removing oxygen mass from quantified TDS concentrations), assuming the sulfide does not precipitate (a conservative assumption)* -- in other words, the system will either produce highly toxic H2S gas when the sulfide does not precipitate, or the TDS standards will be exceeded by the precipitation of sulfide (I assume with Fe). And of course sulfide is toxic to the bugs as well as Amec crews going around trying to sample wells --

If iron sulfides precipitate, they are removed from the groundwater, and so would not be part of the TDS.

OK, first off, I've dealt with a lot of sites under strong sulfate-reducing conditions, and I've never seen safety issues with monitoring wells. It's not like people are sticking their faces up to the MW pipe and breathing in….. If it's that much of a concern, just bring a gas meter and test the AIR (ie not down in the MW, where you are not sticking your face) as you are testing and monitoring wells. My thought is that AMEC is trying to use safety as an excuse to get out of sampling. Sorry, but people sample anaerobic environments all the time, with no special PPE and no problems.

Second, sulfate-reducers produce sulfide gas all the time, and they live around it all the time. Often, sulfide-oxidizing bacteria are happy to see the sulfide, as it's their source material! These sulfide-oxidizers help keep H2S levels in check. I've cultured SRB's in tiny little serum bottles and as long as they had a carbon source, they stayed alive with no problem – and I'm talking for years on end, inside this tiny sealed bottles where the H2S had no way to escape. Here in the wide-open environment, the H2S is going to quickly dissipate, be used up biologically, or get bound up via abiotic reactions with iron. So I'm having a hard time buying the whole argument that sulfide levels are going to become so high in the environment that the poor, fragile SRBs are going to die off.

The potential problems with sulfide are mentioned by Amec in the work plan, and in various other sulfate reduction publications. Inhibition of sulfate reduction in the absence of iron has been found (Beller et al., Microbial degradation of toluene under sulfate-reducing conditions and the influence of iron on the process, Applied Environmental Microbiology, 58(3):786-793, 1992). Just like they haven't proven that there is a microbial population present that can degrade benzene using sulfate, they also have not shown that there are bugs present that would eat the sulfide that would be produced. So the question becomes is there enough iron present in this system to react with all the sulfate they plan to inject (840 tons, injected at a concentration of 320,000 milligrams per liter)? I don't believe anywhere near this amount of sulfate has been injected at other EBR sites for us to have any idea what will happen under these conditions if the sulfate reducing bugs survive the shock loading.

Sure bugs acclimate (or mutate) to high sulfate concentrations, but what about shocking a system that is used to ~ 300 mg/L with concentrations 100,000 time that? How long will it take for an active population to form? Remember we have like 20 years and something north of 400,000 gallons of jet fuel.

I don't know what the bugs will do, or what bugs are already present, or what the ramp-up time for a useful population would be. They probably could do a lab study which would give an idea, or just start the field effort and find out in a few months or a year. But the idea of injecting high concentrations of sulfate is to get useful sulfate concentrations downgradient of the injection points; eventually, sulfate even immediately around the injection points will be lowered to much lower concentrations.

Yep, if you shock a system with 100,000 times of any component, you're running a risk of killing things off. That's on top of the abiotic reactions that would be occurring. The first step, in my opinion, is to figure out if sulfate is even needed by the indigenous microbes. The next step is to then figure out how much sulfate would be needed and where. Some basic biogeochemical testing would answer all of this, in under a couple of months (including lab turn-around times). This is why I've been fighting for some basic baseline data to be obtained and properly analyzed.

My understanding is that it's much easier make things grow in a microcosm than in the field, I would think that a proper field test would be a better proposal – although the microcosms might answer the basic question of whether the bugs at this site will even degrade benzene with sulfate.

The ESTCP document we circulated earlier states, ***"a practical limit for nitrate or sulfate introduction is around 80 mg/L. . . . the practical limit for sulfate introduction is based on the fact that sulfate reduction can result in the accumulation of sulfide, which is inhibitory to many biodegradation processes."***

High sulfide can be inhibitory to microbes (and human beings!), so that is a potential factor. As far the 80 mg/L "practical limit", Line 344 of the Draft_Final_ST012_RD-RAWP_Addendum2.pdf indicates that "Historical groundwater monitoring upgradient of site contamination has shown background sulfate concentrations generally range from 250 to 300 milligrams per liter..." so we're well past 80 mg/L already. But all of the potential problems would require significant monitoring and tweaking as the EBR implementation proceeds – which brings us to the next point...

A phased approach to EBR is proposed, in part, to allow for adjustments to be made in response to remediation system behaviors that differ from modeled approaches. Right. Without something very specific in the work plan, Amec will do nothing, just say let's continue to monitor. Even with a well written work plan, there is no guarantee that they will follow it, as we found during SEE. You have admitted also that RPs would rather get stuck in a monitoring phase than to do something active, even when the data doesn't look so promising.

The success of EBR will depend to a large degree on careful implementation, monitoring, and tweaking – as did the "success" of SEE. If the people implementing EBR cannot be depended on to do a good job, then none of comments we provide will make much difference, even if they are incorporated in the workplan.

I agree that AMEC seems to be ignoring instructions, and is instead just doing whatever they want and then asking forgiveness (sort of). This is why, in past documents, I've carefully written guidelines that clearly state what data needs to be obtained and analyzed as baseline data, prior to any implementations. Then, once implementation plans are agreed to, specific monitoring and reporting protocols need to be followed. I think AMEC will need to be watched very carefully, and disciplined hard if they deviate from any agreed-upon plans.

Eleanor, it's doubtful that you have any idea how much Amec has been ignoring instructions, as you haven't been directly involved. They have not asked for any forgiveness.

Certainly I have not covered all the literature on the subject, but I'm not finding anything that says EBR is a good idea when significant NAPL is present.

EBR is not a good idea to deplete large amounts of NAPL of the COCs of interest – unless one has basically unlimited time for the remedy to work. Which is not to say that it cannot possibly work in the short timeframe, but just that it is very highly uncertain. But, if they can actually achieve in three years what Don indicated in the meeting – no LNAPL or sheen in any of the site wells – then that would be very encouraging.

I would like to see them monitor all site wells where LNAPL or COCs have been found in the last five years, as part of the EBR performance monitoring scheme. They can monitor some of

those just annually, though, and of course in a final synoptic round to declare success for EBR, and start MNA (assuming success happens, of course).

EBR is good for a polishing step. If NAPL needs to be degraded, it will just take a lot longer. Thus, I agree with the above. The major thing is to implement EBR correctly and not just toss in some sulfate because some random publication mentions this as a solution to some (ie, not all) sites.

Which is why there is no way we should approve addendum 2 without major, major changes to it - if the Region wants to compromise with the AF and let them do something in the field, then I think we could design a field test for them to do, and justify it within the superfund process (part of an FFS, justified at this point because we never approved sulfate EBR, the work plan we approved still did not specify if it would be O2 or sulfate). No way would I go along with giving them 3 years to see if the NAPL magically disappears – I'm certain Amec could magically disappear in that time.

Wayne Miller
Arizona Department of Environmental Quality,
Waste Programs Division,
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